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Assessment of Dimethyl Terephthalate  
as a Potential Air Pollution Problem  
Volume XII

GCA Corp, Bedford, Mass GCA Technology Div

Prepared for

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| 16. ABSTRACT<br><br>This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:<br><br><table border="0"> <tbody> <tr> <td>Volume I</td> <td>Acetylene</td> <td>Volume VIII</td> <td>Formaldehyde</td> </tr> <tr> <td>Volume II</td> <td>Methyl Alcohol</td> <td>Volume IX</td> <td>Methyl Methacrylate</td> </tr> <tr> <td>Volume III</td> <td>Ethylene Dichloride</td> <td>Volume X</td> <td>Ortho-Xylene</td> </tr> <tr> <td>Volume IV</td> <td>Benzene</td> <td>Volume XI</td> <td>Maleic Anhydride</td> </tr> <tr> <td>Volume V</td> <td>Acetone</td> <td>Volume XII</td> <td>Dimethyl Terephthalate</td> </tr> <tr> <td>Volume VI</td> <td>Acrylonitrile</td> <td>Volume XIII</td> <td>Adipic Acid</td> </tr> <tr> <td>Volume VII</td> <td>Cyclohexanone</td> <td>Volume XIV</td> <td>Phthalic Anhydride</td> </tr> </tbody> </table> |                                                          |                                                                                                  | Volume I               | Acetylene | Volume VIII | Formaldehyde | Volume II | Methyl Alcohol | Volume IX | Methyl Methacrylate | Volume III | Ethylene Dichloride | Volume X | Ortho-Xylene | Volume IV | Benzene | Volume XI | Maleic Anhydride | Volume V | Acetone | Volume XII | Dimethyl Terephthalate | Volume VI | Acrylonitrile | Volume XIII | Adipic Acid | Volume VII | Cyclohexanone | Volume XIV | Phthalic Anhydride |
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| Dimethyl Terephthalate<br>Ambient Concentrations<br>Measurement Methods<br>Emission Sources<br>Emission Controls<br>Industrial Chemicals<br>Physical Properties                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Health Effects<br>Chemical Properties<br>Welfare Effects | Dimethyl Terephthalate<br>Air Pollution Assessment<br>Air Pollution Control<br>Organic Chemicals |                        |           |             |              |           |                |           |                     |            |                     |          |              |           |         |           |                  |          |         |            |                        |           |               |             |             |            |               |            |                    |
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ASSESSMENT OF DIMETHYL TEREPHTHALATE  
AS A POTENTIAL AIR POLLUTION PROBLEM  
Volume XII

by

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## ABSTRACT

This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

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## SECTION I

### SUMMARY AND CONCLUSIONS

Dimethyl terephthalate is a white crystalline solid. It is manufactured by the oxidation of para-xylene to terephthalic acid, with subsequent methanol esterification. Dimethyl terephthalate is used almost exclusively in the production of polyester fibers and polyester films.

Data on human health effects from dimethyl terephthalate are lacking, and there is no standard for occupational exposures. Contact with dust may be slightly toxic only at high doses. No effects on vegetation have been documented.

Simple conservative diffusion modeling estimates place the likely maximum 1-hour average ambient concentration at  $8.34 \text{ mg/m}^3$  (1.05 ppm). The maximum 24-hour average ambient concentration might be expected to be about  $4.63 \text{ mg/m}^3$  (0.58 ppm). Dimethyl terephthalate is usually found in air as a dust.

Almost 3 billion pounds of dimethyl terephthalate were produced at seven locations in 1974, and production is expected to increase at over 8 percent per year through 1979. The primary emission sources are production and end-product manufacture. Total emissions are estimated to have been about 18 million pounds in 1974.

Emission control methods and reported efficiencies are:

- Scrubbers 93.8 to 99.4 percent
- Bag filters Almost 100 percent
- Incinerators 99 percent

Based on the results of the health effects research presented in this report, and the ambient concentration estimates, dimethyl terephthalate as an air pollutant apparently does not pose a threat to the health of the general population. In addition, dimethyl terephthalate does not appear to pose other environmental insults which would warrant further investigation or restriction of its use at the present time.

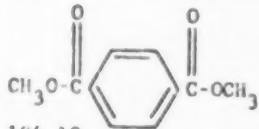
## SECTION II

### AIR POLLUTION ASSESSMENT REPORT

#### PHYSICAL AND CHEMICAL PROPERTIES

Dimethyl terephthalate (DMT) is a white crystalline solid. It is manufactured by the oxidation of para-xylene to terephthalic acid, with methanol esterification to DMT. DMT is a key chemical intermediate in the manufacture of polyester fibers and films. Derivatives are found in coating compositions, insulation, paint and varnish, magnet wire, plasticizers, antifoam agents, and specialty lubricants.<sup>1</sup> Significant properties are given in Table 1.

Table 1. SIGNIFICANT PROPERTIES OF  
DIMETHYL TEREPHTHALATE

| Synonym               | DMT                                                                                  |
|-----------------------|--------------------------------------------------------------------------------------|
| Chemical formula      |  |
| Molecular weight      | 194.18                                                                               |
| Boiling point         | 285°C                                                                                |
| Melting point         | 140.6°C                                                                              |
| Specific gravity      | 1.04                                                                                 |
| Vapor pressure        | 10 mm Hg at 142°C<br>100 mm Hg at 208°C                                              |
| Solubility            | 0.3 g/100 ml hot water                                                               |
| Flash point           | 151°C (closed cup)<br>145°C (open cup)                                               |
| At 25°C and 760 mm Hg | 1 ppm = 7.937 mg/m <sup>3</sup><br>1 mg/m <sup>3</sup> = 0.126 ppm                   |

## HEALTH AND WELFARE EFFECTS

### Effects on Man

The effects of DMT on man have not been well documented in the literature. Its low vapor pressure would tend to prevent any appreciable intake by vapor inhalation.<sup>2,3</sup> Eye or skin contact with the dust may cause slight, transient irritation. Based on studies done on animals, oral ingestion would be slightly toxic only at high levels. No adverse health effects were seen in workers in a factory with air contaminated with DMT.<sup>4</sup> A standard for occupational exposure has not been established; however, care must be taken to avoid prolonged or excessive contact because of its irritating properties.

### Effects on Animals

Acute Poisoning - DMT dust at high levels,  $86.4 \text{ mg/m}^3$  (10.9 ppm), can act as a mild nasal and eye irritant.<sup>3</sup> Oral doses as high as 6590 mg/kg given to rats caused no deaths. The intraperitoneal  $\text{LD}_{50}$  was 3900 mg/kg, with all deaths occurring within 48 hours after injection. Slight-to-moderate weakness was seen at all dose levels regardless of the method of administration. At the two highest oral dose levels, 5020 and 6590 mg/kg, there were slight tremors and some ataxia. Autopsies revealed no gross microscopic abnormalities in the organ systems of the animals.

A quantity of 0.5 ml of a 1 percent DMT solution dropped on the rump area of guinea pigs caused no primary irritation. It was found not to be a skin sensitizer.<sup>5</sup> Moistened DMT in contact with the depilated skin of guinea pigs caused only slight skin irritation with no evidence of direct absorption through intact skin.<sup>1</sup> One drop of a water slurry placed in the conjunctival sac of a rabbit's eye resulted in only slight, immediate discomfort, with no permanent injury resulting.

Chronic Poisoning - Rats exposed to  $86.4 \text{ mg/m}^3$  (10.9 ppm) DMT dust for 4 hours per day for 58 exposures started nose rubbing, preening and blinking soon after the start of exposure. The symptoms continued intermittently throughout the exposure period and were seen in the successive exposures. Exposure to  $16.5 \text{ mg/m}^3$  (2.1 ppm) for the same duration and frequency produced no toxic effects or abnormal behavior. Microscopic examination of all organ systems showed no evidence of any abnormalities.

Feeding rats at a 5 percent level in the daily diet (3.75 g/kg daily) for 28 days resulted in a loss of weight, a marked reduction of food consumption, and high mortality.<sup>5</sup> Rats fed at a 1 percent level in their daily diet for 96 days showed a significant reduction in average body weight as compared to controls.<sup>3</sup> The mechanism of the effects of DMT on rats is unknown.

#### Effects on Vegetation

The effect of DMT on vegetation has not been documented in the literature.

#### Other Effects

When DMT is heated, it will sublime and can form a potentially explosive dust. The flash point is  $146^\circ\text{C}$  by the open cup method. Contact with strong oxidizing agents will cause a chemical reaction.<sup>6</sup>

### AMBIENT CONCENTRATIONS AND MEASUREMENTS

#### Ambient Concentration Estimates

The largest installation for dimethyl terephthalate production is located near a town of about 50,000 population, and it has a capacity of about 1,300 million lb/yr. Assuming a 0.3 percent loss, this converts to an emission rate of:

$$\frac{(0.003 \text{ emission factor}) (1300 \times 10^6 \text{ lb/yr}) (453.6 \text{ g/lb})}{3.1536 \times 10^7 \text{ sec/yr}}$$

= 56.1 g/sec of dimethyl terephthalate.

Some assumptions must be made regarding this dimethyl terephthalate release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations within the plant. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed. Thirdly, it is assumed that these emissions are in the form of particulate small enough to behave as a gas (of the order of 10  $\mu\text{m}$ ).

Ground level concentrations can then be estimated at locations downwind of the facility.<sup>7</sup> To do this a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{y0} = 100 \text{ m}/4.3 = 23.3 \text{ m}.$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from:

$$X = \frac{Q}{u \pi \sigma_y \sigma_z} \exp \left[ -1/2 \left( \frac{H}{\sigma_z} \right)^2 \right]$$

or

$$X = \frac{56.1}{(2)\pi(36)(18.5)} \exp \left[ -1/2 \left( \frac{10}{18.5} \right)^2 \right]$$
$$= 11.58 \text{ mg/m}^3$$

for a 10-minute average concentration. Over a period of an hour this becomes  $11.58 \text{ mg/m}^3 (0.72) = 8.34 \text{ mg/m}^3 (1.05 \text{ ppm})$  1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about  $4.63 \text{ mg/m}^3 (0.58 \text{ ppm})$ .

#### Dimethyl Terephthalate Measurement Techniques

Dimethyl terephthalate present as an airborne particulate should be collected on a Whatman No. 1 filter paper or on a glass filter. For the collection of vapor or fumes, two gas washing bottles or bubblers in series containing spectrographic grade 3-A alcohol are used.<sup>8</sup>

One method, which has a high degree of sensitivity for measuring dimethyl terephthalate, is collecting the sample using bubblers or filter paper, with the subsequent extraction of the particles from the filter paper with a suitable solvent. The absorbence of the sample is measured in an ultraviolet spectrophotometer at 225 mμ and then compared to a standard calibration curve. Interferences will result from other aromatic substances present in the sample. A 1-cubic foot air sample will allow detection to 0.02 ppm.<sup>8</sup>

#### SOURCES OF DIMETHYL TEREPHTHALATE EMISSIONS

##### Dimethyl Terephthalate Production and Consumption

The production of dimethyl terephthalate (DMT) is estimated to have been 2,953 million pounds in 1974, and it is expected to increase at 8.2 percent

per year through 1979.<sup>9</sup> Dimethyl terephthalate is used almost exclusively to produce polyester fibers and polyester films. In 1973 about 73 percent of all polyester fibers produced in the United States were based on DMT. The production of polyester films for magnetic tapes, photographic films and packaging applications accounted for almost the remainder of the total production. Five companies at seven locations are presently producing dimethyl terephthalate. See Appendix A for names and locations.

The consumption of dimethyl terephthalate for final products is shown in Table 2. This table also shows the expected growth rate for each sector of the market.

Table 2. DIMETHYL TEREPHTHALATE CONSUMPTION - 1974<sup>9</sup>

| Product                           | Millions of pounds | Annual % growth |
|-----------------------------------|--------------------|-----------------|
| Polyester fiber                   | 2726               | 8.0             |
| Polyester film                    | 207                | 9.0             |
| Polybutylene terephthalate resins | 15                 | 38.0            |
| Miscellaneous                     | 5                  | 5.0             |
| Total                             | 2953               | 8.2             |

#### Dimethyl Terephthalate Sources and Emission Estimates

Primary sources of emissions of dimethyl terephthalate occur from production, end-product manufacture, and storage. Total emissions of dimethyl terephthalate are estimated to have been 17.83 million pounds in 1974, representing 0.6 percent of total production. See Table 3.

Table 3. SOURCES AND EMISSION ESTIMATES OF  
DIMETHYL TEREPHTHALATE - 1974

| Source                                      | Emissions,<br>million pounds/year |
|---------------------------------------------|-----------------------------------|
| Dimethyl terephthalate<br>production losses | 8.9                               |
| End-product losses                          | 8.9                               |
| Storage                                     | 0.03                              |
| Total                                       | 17.83                             |

The major sources of emissions of dimethyl terephthalate occur from production and end-product losses. Three processes are currently being used to manufacture DMT: Dupont Process, Tennessee Eastman Process, and the Hercules Process. The Dupont Process, which is generally considered obsolete, begins with para-xylene, which is oxidized with nitric acid to para-toluic acid. It is further treated under pressure and converted to terephthalic acid, which is then esterified to DMT. This process is still being used by Dupont at one of their production sites.

The Tennessee Eastman Process is also based on para-xylene feedstock and a crude terephthalic acid intermediate. Para-xylene is oxidized at a low temperature and pressure with acetic acid solvent, a cobalt acetate catalyst, and an acetaldehyde activator. The crude terephthalic acid is then esterified with methanol to produce DMT.

The Hercules Process, which accounts for the bulk of DMT production, is based on Witten-Imhausen technology. Para-xylene is oxidized with air under mild operating conditions to produce toluic acid, which is esterified to its methyl ester. The methyl toluate is oxidized under more severe conditions to monomethyl terephthalate which is then esterified to form DMT.

Emissions data for these processes are not readily available in the literature; however, data for the production of terephthalic acid (TPA) do exist, and because of the similarity between the processes, these will be used in estimating production losses of DMT.<sup>10</sup>

In a recent report concerning emissions from the production of TPA, it was estimated that approximately 0.3 percent of production is lost in the form of TPA. Using this report as a basis, it is estimated that production losses from DMT production will also be 0.3 percent. Using 2953 million pounds as the most recent production figure, losses are estimated to be 8.9 million pounds.

Since emission data from the use of DMT are not readily known, it is assumed that end-product losses are also 8.9 million pounds.

Emissions from product storage and handling are estimated to be  $10^{-5}$  pounds of DMT emitted per pound of DMT transported.<sup>10</sup> This results in 0.03 million pounds of DMT powder lost from storage and handling.

#### DIMETHYL TEREPHTHALATE EMISSION CONTROL METHODS

Three types of control devices are currently being used by the chemical industry: scrubbers, bag filters, and incinerators. A recent study<sup>10</sup> indicated that these three control methods are used extensively in the manufacture of terephthalic acid. It is assumed that these three methods are also used in the production of dimethyl terephthalate.

The bag filter is reported to have an efficiency approaching 100 percent. The incinerator is reported to combust organic acids and methanol with an efficiency of 99 percent and the scrubber has a reported efficiency of from 93.8 to 99.4 percent. Cost data<sup>10</sup> for the various systems are presented in Tables 4, 5, and 6.

Table 4. ABSORBER/SCRUBBER<sup>a</sup> FOR CONTROL OF  
HYDROCARBON EMISSIONS<sup>10</sup>

|                                     |             |
|-------------------------------------|-------------|
| Design temperature                  | 120°F       |
| Gas rate                            | 32,150 scfm |
| Installed cost - material and labor | \$147,000   |
| Annual operating cost               | \$117,800   |
| Value of recovered product          | \$479,800   |
| Net operating cost - annual profit  | \$362,000   |
| Efficiency                          | 93.8-99.4%  |

<sup>a</sup>Costs updated to first quarter 1975.

Table 5. BAG FILTERS<sup>a</sup> FOR CONTROL OF  
TEREPHTHALIC ACID<sup>10</sup>

|                                     |          |
|-------------------------------------|----------|
| Design temperature                  | 275°F    |
| Installed cost - material and labor | \$39,750 |
| Annual operating cost               | \$ 6,450 |
| Efficiency                          | ≈ 100%   |

<sup>a</sup>Costs updated to first quarter 1975.

Table 6. INCINERATOR<sup>a</sup> WITH WASTE HEAT BOILER<sup>10</sup>

|                                     |                               |
|-------------------------------------|-------------------------------|
| Type of compounds incinerated       | Organic acids<br>and methanol |
| Quantity incinerated                | 40 gpm                        |
| Auxiliary fuel                      | Fuel oil                      |
| Rate                                | 126 gph                       |
| Stack height                        | 100 feet                      |
| Installed cost - material and labor | \$987,200                     |
| Annual operating cost               | \$214,550                     |
| Value of heat/steam recovered       | \$106,600                     |
| Net annual operating cost           | \$107,950                     |
| Efficiency                          | 99%                           |

<sup>a</sup>Costs updated to first quarter 1975.

### SECTION III

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APPENDIX A  
MANUFACTURERS OF DIMETHYL TEREPHTHALATE<sup>9</sup>

|                        |                          | <u>Annual capacity,<br/>million pounds</u> |
|------------------------|--------------------------|--------------------------------------------|
| American Hoechst Corp. | Spartanburg, S. Carolina | 160                                        |
| Amoco Chemicals Corp.  | Decatur, Alabama         | 200                                        |
| Amoco Chemical Corp.   | Joliet, Illinois         | 150                                        |
| Dupont                 | Wilmington, N. Carolina  | 750                                        |
| Dupont                 | Old Hickory, Tenn.       | 300                                        |
| Eastman Kodak Co.      | Kingsport, Tenn.         | 400                                        |
| Hercules Incorporated  | Wilmington, N. Carolina  | <u>1,300</u>                               |
|                        | Total                    | <u>3,260</u>                               |